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Water-Related Environmental Fate of 129 Priority Pollutants. Volume I:  
Introduction and Technical Background, Metals and Inorganics, Pesticides  
and PCBs

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13. LEAD

13.1 Statement of Probable Fate

Sorption processes are effective in reducing the concentration of soluble lead in natural waters and result in enrichment of bed sediments near the source. The equilibrium solubility of lead with carbonate, sulfate, and sulfide is low. In severely contaminated areas, precipitation may be important in controlling the mobility of this metal, but under most circumstances, sorption predominates. The tendency for lead to form complexes with naturally occurring organic materials (e.g., humic and fulvic acids) increases its adsorptive affinity for clays and other mineral surfaces. Benthic microbes can methylate lead to form tetramethyl lead which is volatile and more toxic than inorganic lead. Biomethylation may, in this manner, also provide a mechanism for remobilization of lead in the bed sediments. Bioaccumulation of weakly sorbed lead phases also may result in remobilization. Lead is generally not biomagnified; bioconcentration factors tend to decrease as the trophic level increases.

13.2 Identification - Geochemistry of Lead

Lead is a naturally occurring element and is a major constituent of more than 200 identified minerals. Most of these are very rare, and only three are found in sufficient abundance to form mineable deposits: galena (PbS) the simple sulfide, anglesite (PbSO<sub>4</sub>) the sulfate, and cerussite (PbCO<sub>3</sub>) the carbonate. By far the most abundant is galena which is the primary constituent of the sulfide ore deposits from which most lead is presently mined.

Ores of lead, as well as those of zinc, are often closely associated in deposits formed by replacement of limestone or dolomite. Lead ore is commonly present together with ores of copper, zinc, silver, arsenic, and antimony in complex vein deposits, but lead ore also may occur in a variety of igneous, metamorphic, and sedimentary rocks.

Lead, atomic number 82, atomic weight 207.19, is a member of the group IV elements (Weast 1977). Lead exists in three oxidation states, 0, +2, and +4. Although neither metallic lead nor the common lead minerals is classified as soluble in water, they can both be solubilized by some acids; in contrast, some of the lead compounds produced industrially are considerably water soluble. Therefore, natural compounds of lead are not usually mobile in normal ground or surface water because the lead leached from ores becomes adsorbed by ferric hydroxide or tends to combine with carbonate or sulfate ions to form insoluble compounds (Hem 1976a).

The average abundance of lead in the earth's crust is approximately ppm (Lovering 1976) which is equivalent to one-half ounce of lead per ton of rock. Shales and unconsolidated sediments have a mean lead abundance close to the crustal average, showing the fairly even distribution of lead in the environment.

The CAS number for lead is 7439-92-1; the TSL number is B049-0641.

### 13.3 Summary of Fate Data

#### 13.3.1 Photolysis

Although no evidence was found concerning the photolysis of organo-lead complexes in natural waters, photolysis of these compounds in the atmosphere has a great bearing on the form of lead which will enter the aquatic environment. For example, Hirschler and Gilbert (1964) report that the chief constituents of the inorganic lead compounds leaving the exhaust system of automobiles burning leaded fuels are two forms of  $PbClBr$ ,  $NH_4Cl \cdot 2PbClBr$  and  $2NH_4Cl \cdot PbClBr$ . The species  $PbClBr$  (lead bromochloride) appears to be stable at ordinary temperatures and is isomorphous with  $PbCl_2$  and  $PbBr_2$ . Both  $PbCl_2$  and  $PbBr_2$  darken on exposure to sunlight with the release of halogen. The ultimate products of the photolysis of these lead compounds in the atmosphere would be  $PbO$  and the halogens. Since the majority of the lead emitted to the environment originates from the tailpipes of automobiles, these photolytic processes are quite important. Also of importance, as Pierrard (1969) has pointed out, is that the halogens produced from the photolysis of the lead halides may be involved in chain reaction mechanisms with such atmospheric pollutants as  $CO$ ,  $NO$ , and  $SO_2$ .

#### 13.3.2 Chemical Speciation

An outstanding characteristic of lead is its tendency to form complexes of low solubility with the major anions of natural environmental systems. The hydroxide, carbonate, sulfide, and (more rarely) the sulfate of lead may act as solubility controls. Throughout most of the natural environment, the divalent form,  $Pb^{+2}$ , is the stable ionic species of lead. The more oxidized solid  $PbO_2$ , in which lead has a +4 charge, is stable only under highly oxidizing conditions, and probably has very little significance in the aquatic environment (Cotton and Wilkerson 1972). If sulfur activity is very low, metallic lead can be a stable phase in alkaline or circumneutral reducing conditions.

Huang *et al.* (1977) calculated the equilibrium solubility of lead as a function of  $pE$  for a system with total carbonate and total sulfur concentrations of  $10^{-3}$  M at pH 7. Figure 13-1 shows the solubility of lead

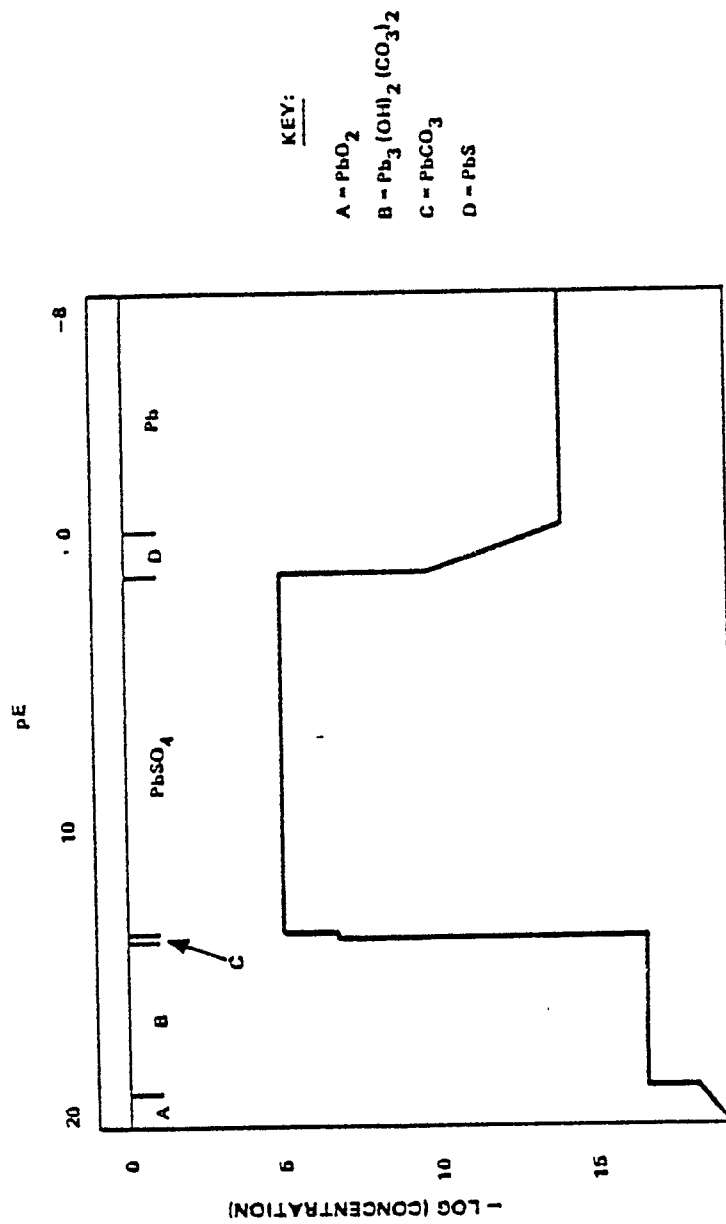


Figure 13-1 Solubility of lead as a function of pE. Modified from Huang et al. (1977).

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and the controlling solid species for pE from +20 to -8. At pH 7,  $\text{PbSO}_4$  controls solubility over much of the pE range encountered in natural waters.

Hem (1976b) calculated the fields of stability for solid species of lead based on the available thermodynamic data; these results are summarized in Figure 13-2 and Figure 13-3. Although these figures are useful in depicting equilibrium behavior, they are limited in that they do not take into account environmental interactions with organic compounds and other trace elements and, therefore, may be misleading with respect to fate and transport in normal surface waters. Hem (1976a) looked at the equilibrium distribution between lead in solution and lead adsorbed on cation exchange sites in sediments. He calculated these distributions using equations representing selectivities of substrate for lead over  $\text{H}^+$ ,  $\text{Ca}^{+2}$ , and  $\text{Na}^+$  and the stabilities of lead solute species. Included in the calculations were total concentrations of major ions, cation exchange capacity of the substrate, and pH. The cation exchange behavior of lead in natural systems could be predicted with this model if enough supporting information were available. The available information for describing natural stream sediments, however, is inadequate for accurate use of this model. In general, Hem's model suggests that in most natural environments, sorption processes would more effectively scavenge dissolved lead than precipitation.

Long and Angino (1977) developed a theoretical model to study the chemical speciation of lead in aquatic environments and the response of lead to variations in ionic strength and complexation. Association of lead with the ligands  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{-2}$ ,  $\text{SO}_4^{-2}$ , and  $\text{HCO}_3^-$  was considered at pH values from 3.5 to 11.0 at 25°C in differing seawater-freshwater mixtures. The results are summarized in Figure 13-4. In general, the relative importance of the various ligand-lead complexes can be predicted from a comparison of their stability constants; however, since this model does not take into account metal-organic complexes, it is useful only in unpolluted, relatively organic-free waters.

Dissolved lead may be hydrolyzed to form  $\text{Pb}(\text{OH})_2$ . Patterson et al. (1977) studied the formation of  $\text{Pb}(\text{OH})_2$  versus  $\text{PbCO}_3$  to determine the feasibility of treating lead-containing waters with carbonates. They found that  $\text{PbCO}_3$  controls lead solubility at  $\text{pH} < 11.5$ . Even small concentrations of inorganic carbonate due to dissolution of atmospheric  $\text{CO}_2$  are sufficient to reduce the solubility of lead to concentrations below those predicted on the basis of hydrolysis alone. It should be noted that lead concentrations were reduced nearly to the computed solubility limits within four hours; thus, precipitation of lead carbonate can occur quickly.

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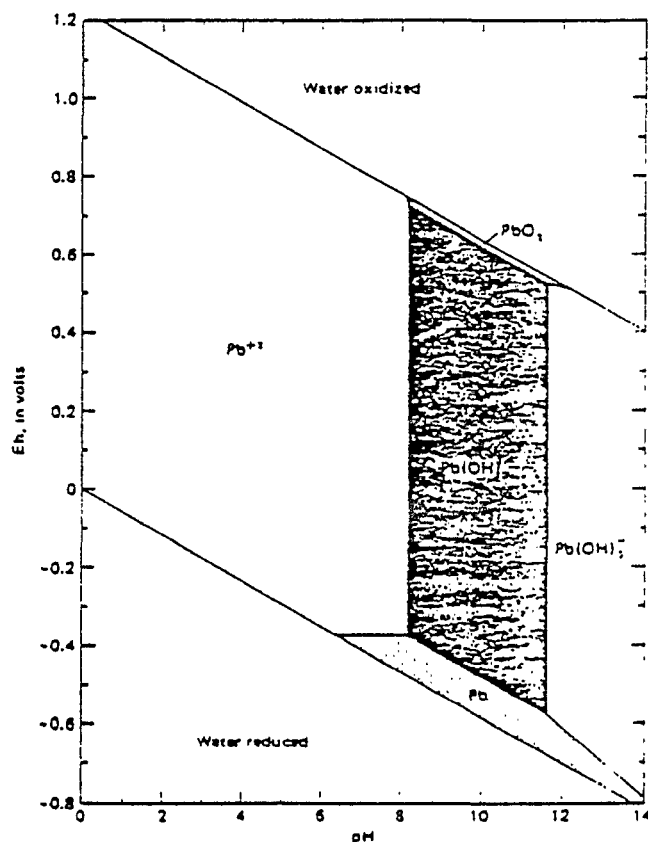


Figure 13-2 Fields of stability for solid species and dominant solute species in system  $\text{Pb} + \text{H}_2\text{O}$  as functions of pH and redox potential. Dissolved lead activity is  $10^{-8.32}$  mol/l at  $25^\circ\text{C}$  and 1 atm. pressure. From Hem (1976b).

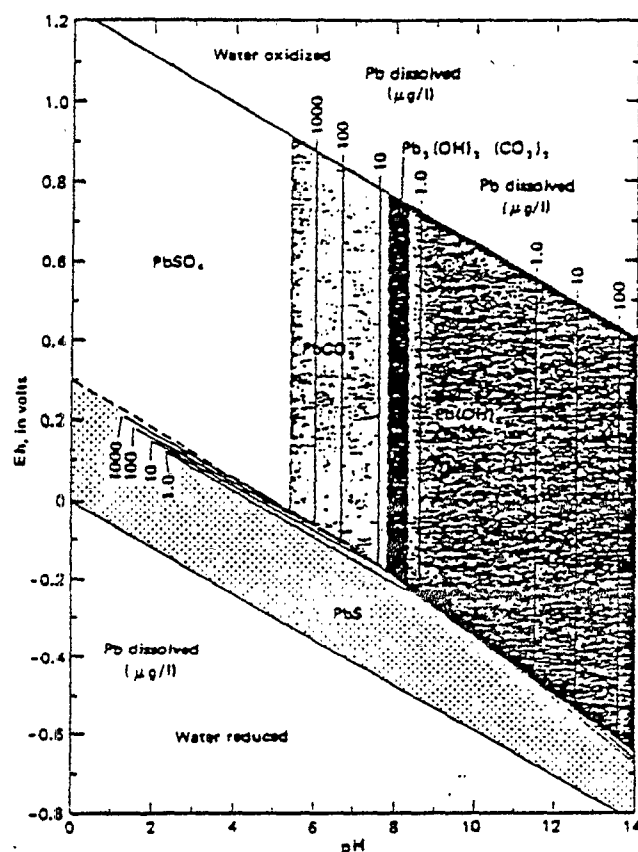


Figure 13-3 Fields of stability for solids and solubility of lead in system  $Pb + CO_2 + S + H_2O$  at  $25^\circ C$  and 1 atm. pressure. Ionic strength 0.005. From Hem (1976b).

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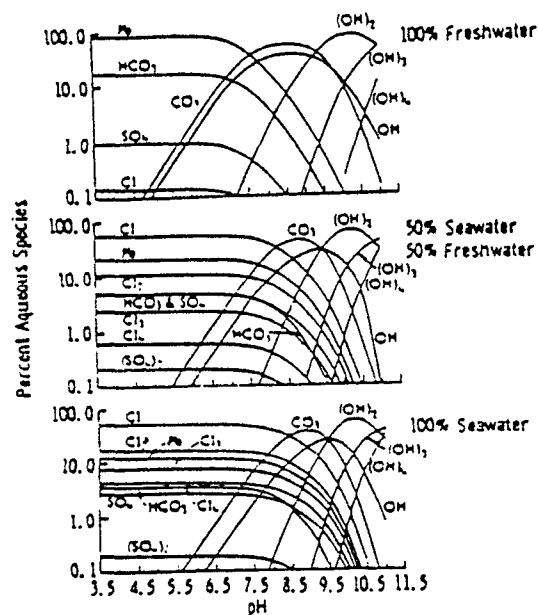


Figure 13-4 Chemical speciation of lead in seawater-freshwater mixtures. From Long and Angino (1977).



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At the low concentration in which lead is normally found in the aquatic environment, almost all of the lead in the dissolved phase may be complexed by the ligands of river water. By using an ion-specific electrode, Ramamoorthy and Kushner (1975) determined that lead binding capacity was predominantly due to organic compounds. Inorganic complexes were not important, since evaporating the water samples, ashing the residue, and reconstituting the ash in water resulted in complete loss of the binding capacity. (In waters with a high carbonate concentration, however, binding by  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  is important).

Guy and Chakrabarti (1976), in their study of metal-organic interactions in natural waters, found that humic acids in solution and other organic complexing agents can maintain lead ions in a bound form at a pH as low as 3. O'Shea and Mancy (1978), in their study of the effect of pH and hardness on lead speciation, found that the effects of pH and hardness metals were insignificant in lead-inorganic interactions. They were important, however, in lead-humic acid interactions. Increasing the pH increased the concentration of exchangeable lead complexes while an increase in hardness tends to decrease the extent of the humic acid-lead interaction. Metals responsible for hardness apparently inhibit the exchangeable interactions between metals and humic materials in ways that are not fully understood.

Jackson and Skippen (1978) investigated the behavior of lead and organic materials at a simulated sediment-water boundary. The interactions involved sorption by clays, organic complexing, carbonate reactions, hydrolysis, and desorption of lead from clay and metal hydroxides. They found that organic acids decreased the solubility of lead in the presence of clay, particularly at acidic pH values. This organic complexing is probably due to colloidal coagulation. The organic acids, moreover, proved capable of remobilizing lead from the solid phase. There is, however, a general kinetic hindrance to this desorption, particularly at basic pH values.

In summation, the transport of lead in the aquatic environment is influenced by the speciation of the ion. Although lead will exist mainly as the divalent cation in most unpolluted waters and become sorbed into particulate phases, organic material in polluted waters will have a great effect on the chemical form in which lead will be present.

### 13.3.3 Volatilization

The relatively volatile tetramethyl lead  $((\text{CH}_3)_4\text{Pb})$  can be produced by microorganisms in lake sediments from inorganic  $(\text{Pb}(\text{NO}_3)_2$  and  $\text{PbCl}_2)$  and organic  $((\text{CH}_3)_3\text{PbOOCCH}_3)$  lead compounds (Wong *et al.* 1975). Analysis of air in flasks that contained anaerobic lake sediments

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inoculated with these compounds showed that tetramethyl lead thus produced can be volatilized. Under these experimental conditions, addition of 10 mg of lead as trimethyl lead acetate resulted in volatilization of weekly increments of 125  $\mu$ g, 642  $\mu$ g, 550  $\mu$ g, and 256  $\mu$ g of tetramethyl lead during the first four weeks (Wong et al. 1975). Nevertheless, the importance of volatilization of tetramethyl lead is uncertain. Although the rate of destruction of tetramethyl lead in aerobic waters is unknown, this compound is probably not stable in oxidizing environments. When a layer of aerobic water lies between the reducing sediments and the atmosphere, volatilization may not be important.

#### 13.3.4 Sorption

Sorption processes appear to exert a dominant effect on the distribution of lead in the environment. Several investigators have reported that in aquatic and estuarine systems, lead is removed to the bed sediments in close proximity to its source, apparently due to sorption onto the sediments (Helz et al. 1975; Valiela et al. 1974). Different sorption mechanisms have been invoked by different investigators, and the relative importance of these mechanisms varies widely with such parameters as geological setting, pH, Eh, availability of ligands, dissolved and particulate iron concentration, salinity, composition of suspended and bed sediments, and initial lead concentration.

Pita and Hyne (1975) studied the depositional environment of lead in reservoir sediments and found that almost all of the lead in the sediments was in the fraction with specific gravity between 2.0 and 2.9. This fraction contains the clays. The authors suggested that formation of organo-lead complexes may play an important role in adsorption, noting that "the same type of organic matter (negatively charged or polar) which tends to form organo-metallic compounds would also tend to adhere to clay minerals and would occur in the 2.0 to 2.9 specific gravity portion." The paucity of lead in sediments with specific gravity less than 2.0 indicated that adsorption onto organic material not active in complex formation was insignificant; the lack of lead in the denser fraction (sp. gr. > 2.9) indicated that precipitation was not important. The relative dominance of adsorption over precipitation is corroborated by calculations made by Hem (1976a), which indicate that precipitation is important only under relatively alkaline conditions.

[ The adsorption of lead to soils and oxides was studied by Huang et al. (1977). The data indicate that adsorption is highly pH-dependent, but above pH 7, essentially all of the lead is in the solid phase (Figure 13-5). It should be noted that at low pH, lead is negatively sorbed (repelled from the adsorbent surface). The addition of organic complexing agents increased the affinity for adsorption (Figure 13-6). Therefore, the

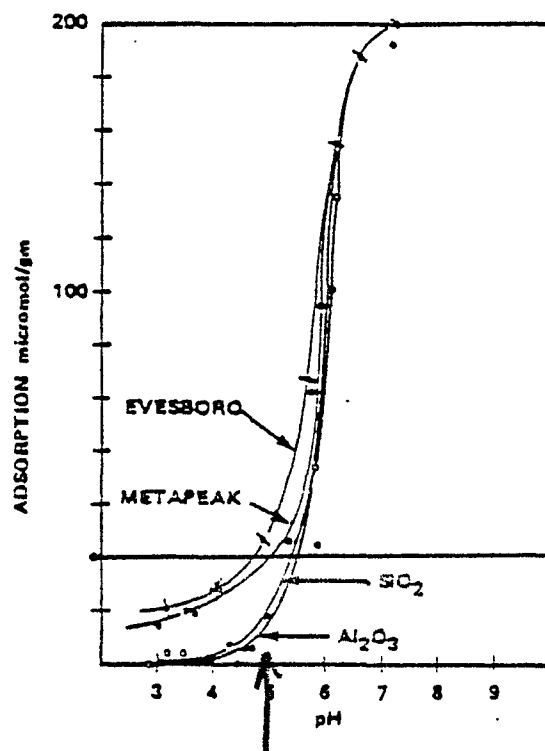


Figure 13-5 Adsorption of lead on various solids. The soil-water system consisted of 5 gm/l solid,  $10^{-3}$ M Pb, and 0.1M NaCl (thus adsorption of 200  $\mu$ M/gm = 100% removal). From Huang et al. (1977).

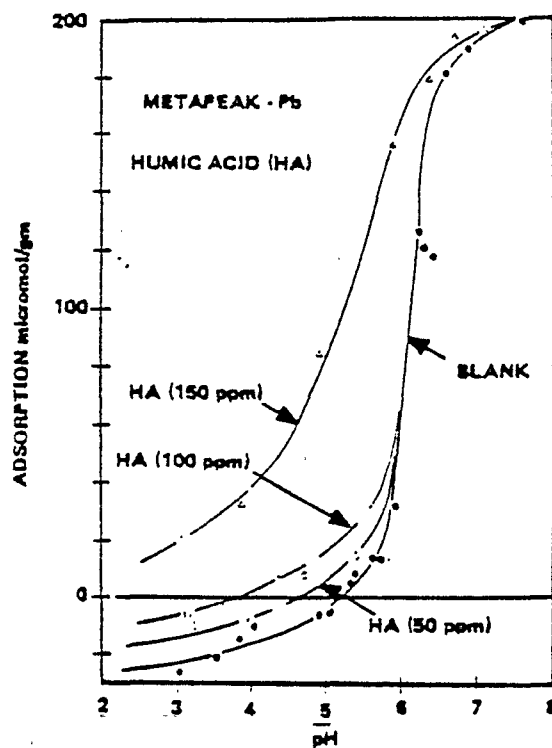


Figure 13-6 Effect of humic acid on the adsorption of lead by metapeak soil. Soil added at 5 gm/l, initial  $[Pb^{2+}] = 10^{-3}M$ , ionic strength =  $10^{-1}M$  (NaCl). From Huang et al. 1977.

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tendency for lead to be adsorbed probably reflects the fact that lead is strongly complexed by organic materials in the aquatic environment (Ramamoorthy and Kushner 1975). Huang *et al.* (1977) speculate that the increased adsorption is due to the ability of the metal-ligand complexes to share free electrons, thus facilitating sorption to electrophilic solid surfaces.

Similar studies have been carried out in seawater environments. For example, Patterson *et al.* (1976), in their study of sewage effluent entering polluted coastal waters, found that virtually all the lead in the sewage was contained in the particulate phase before it entered the ocean but that about 11 percent was made freely available within a day by cation exchange when the sewage was mixed with seawater. Further exposure of the sewage to seawater, however, did not facilitate the release of more lead. Lu and Chen (1977), in their laboratory study of the migration of trace metals from polluted sediment into seawater, found that the release of lead from the sediment increased as the redox conditions became more oxidizing. Moreover, after long-term incubation under aerobic conditions, lead concentrations were far below equilibrium concentration. This latter observation is indicative of the substantial sorption processes which lead undergoes in aquatic sediments.

Ramamoorthy and Rust (1978) found that the sorption of lead by Ottawa River bed sediments can be fitted to the linear form of Langmuir's equations. They reported that the partition coefficient of lead between sediment and solution is not greatly changed by the presence of other heavy metals, provided that the latter has the same order of concentration. If the concentration of one cation exceeds the other by more than a factor of 10, however, significant desorption of the less concentrated ion takes place on a mass action basis.

There are significant differences reported not only in the mode of binding to bed sediments, but also in the distribution of lead among phases in the water column. Some authors report that lead is transported predominantly in the particulate phase rather than the dissolved phase (Kubota *et al.* 1974; Schell and Nevissi 1977); others report that the amount in the dissolved phase is about equal to that in the particulate phase (Angino *et al.* 1974); and still others find that more lead is transported in the dissolved phase than in the suspended material (Pita and Hyne 1975). There is general agreement, however, that residence in lakes and impoundments causes a reduction in dissolved lead levels even when lead is initially present in concentrations below calculated solubility limits (Kubota *et al.* 1974; Pita and Hyne 1975). Thus, sorption processes appear to be effective in reducing dissolved lead levels and result in enrichment of bed sediments. It appears that, under most conditions, adsorption to clay and other mineral surfaces, coprecipitation/sorption by hydrous iron oxides, and incorpora-

tion into cationic lattice sites in crystalline sediments are the important sorption processes.

Several authors, notably Jenne (1968), Lee (1975), and Hohl and Stumm (1976), have hypothesized that the sorption of heavy metals by hydrous iron and manganese oxides is a major control on the mobility of these pollutants in the aquatic environment. On the basis of a high correlation between the lead, iron and manganese concentration in sediments, Angino et al. (1974) suggested that sorption by iron and manganese oxides is the dominant sorption process in several Kansas streams. Gaddie and Laitmen (1973) demonstrated that hydrous iron oxides have a high sorption capacity for lead, sorbing as much as 0.28 moles lead per mole iron at pH 6. The ability of hydrous iron oxides to sorb lead increases with increasing pH. At pH 8.1, 91 percent of the added lead was sorbed. When the pH drops, however, lead may be desorbed. Although the relative importance of individual sorption processes varies widely, it appears that, in most circumstances, lead is effectively removed to the sediments by sorption.

#### 13.3.5 Bioaccumulation

Bioaccumulation of lead has been demonstrated for a variety of organisms. Table 13-1 lists bioconcentration factors reported by various sources.

Microcosm studies indicate that lead is not biomagnified. Lu et al. (1975) studied the fate of lead in three ecosystems differing only in their soil substrate. The ecosystems contained algae, snails, mosquito larvae, mosquito fish, and microorganisms. Lead was concentrated most by the mosquito larvae and least by the fish. Furthermore, body burdens and aqueous lead concentration appeared to be strongly correlated to the percentage of organic matter and cation exchange capacity of the soils, indicating that the availability of lead in the systems was controlled by adsorption to the soils. Since pH was the same for all three soils, precipitation/dissolution of inorganically bound lead was probably not responsible for the differences in lead availability and uptake.

Merlini and Pozzi (1977a) measured lead uptake in pumpkinseed sunfish (Leponis gibbosus) exposed to  $^{203}\text{Pb}$  at pH 6.0 and 7.5. Fish at the lower pH accumulated three times as much lead as fish kept at pH 7.5. Gill, liver, and fin accumulated the most lead and muscle the least. The authors attributed the increased lead uptake at low pH to the increasing concentration of divalent lead with decreasing pH. In another experiment, Merlini and Pozzi (1977b) found a direct correlation between lead accumulation by pumpkinseed sunfish and the concentration of ionic lead in water at various concentrations of total lead. Results suggest that the conditions existing in the majority of natural waters render most lead unavailable for accumulation by aquatic animals.

Table 13-1

Bioconcentration Factors for Lead

<u>Taxon</u>	<u>Bioconcentration Factor<sup>a</sup></u>	<u>Reference</u>
Freshwater plants	200	Chapman <u>et al.</u> 1968
Freshwater invertebrates	200	Chapman <u>et al.</u> 1968
Freshwater fish	60	Chapman <u>et al.</u> 1968
Marine plants	200	Chapman <u>et al.</u> 1968
Marine invertebrates	200	Chapman <u>et al.</u> 1968
Marine fish	60	Chapman <u>et al.</u> 1968

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- a. Bioconcentration factors are the ratio derived from the concentration of the element in the aquatic organism (in ppm wet weight) divided by the concentration of the element in water (in ppm).

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Patrick and Loutit (1976) studied uptake of lead by benthic bacteria and subsequent transfer to tubificid worms. The concentration factor for bacteria was approximately 360. Concentration of lead by tubificids was 0.77 times the amount fed them in the bacteria, indicating that the tubificids can clear lead more easily than the bacteria. The fact that the bacteria could concentrate lead indicates that lead in the sediments can be remobilized by bioaccumulation.

Based upon available information, fish accumulate very little lead in edible tissues; however, oysters and mussels are capable of accumulating high levels of lead. Decreasing pH increases the availability of divalent lead, the principal form accumulated by aquatic animals.

#### 13.3.6 Biotransformation

As previously discussed, lead can be methylated by microorganisms present in lake sediments. The volatile compound resulting from biomethylation, i.e., tetramethyl lead, probably leaves the sediments and is either oxidized in the water column or enters the atmosphere. In any event, biomethylation represents a process which enables lead in the bed sediments to be reintroduced to the aqueous or atmospheric environment. In addition, biogenic ligands can play a significant role in complexing lead, especially in polluted waters, and will thereby have a significant impact on the aquatic fate of lead.

#### 13.4 Data Summary

The dominant mechanism controlling the fate of lead appears to be sorption. Precipitation of  $PbSO_4$ ,  $PbCO_3$ , and  $PbS$  and bioaccumulation may also be important. At low pH values, sorption and precipitation are not nearly as effective in removing lead from solution, so that lead is much more mobile in acidic waters than at higher pH values. In alkaline and circumneutral waters, removal of lead by sorption and precipitation may occur relatively quickly. Table 13-2 summarizes the fate data.



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Table 13-2

Summary of Aquatic Fate of Lead

<u>Environmental Process</u>	<u>Summary Statement</u>	<u>Confidence of Data</u>
Photolysis <sup>a</sup>	Important in determining the form of lead entering the aquatic environment. Importance within natural waters is undeterminable.	Medium
Chemical Speciation <sup>a</sup>	Determines which solid species controls solubility in unpolluted waters. Over most of the normal pH range, $PbCO_3$ and $PbSO_4$ control solubility in aerobic conditions. $PbS$ and $Pb$ control solubility in anaerobic conditions. In polluted waters, organic complexation is most important.	Medium
Volatilization	Probably not important in most aquatic environments.	Medium
Sorption <sup>a</sup>	Adsorption to inorganic solids, organic materials, and hydrous iron and manganese oxides usually controls the mobility of lead.	High
Bioaccumulation <sup>a</sup>	Lead is bioaccumulated by aquatic organisms. Bioconcentration factors are within the range of $10^2 - 10^3$ .	High
Biotransformation <sup>a</sup>	Biomethylation in sediments can re-mobilize lead.	Medium

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- a. All of the noted environmental processes are important; however, their relative importance with respect to each other is uncertain for determining final fate.

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may produce hard, high-sulfate mine drainages having extremely high total dissolved solids. This problem most commonly occurs in the Gulf Coast Province.

Accelerated rock-acid water interactions, resulting from the formation of acidic drainages and lower pH, enhance the chemical decomposition of clays and silicate minerals. In addition to the acidity and the variety of chemical species found with the acid-producing reactions, other elements occurring within the coal and rocks are released from the host material and mobilized by the acidic drainages.

Increased concentrations of major elements (greater than 0.1 percent) such as silica, sodium, aluminum, calcium, iron, magnesium, manganese, copper, and zinc are associated with acidic mine drainages. Because of the depressed pH, the solubility of most of the common minor and trace elements is enhanced and entrained with the mine water. Elements (such as antimony, arsenic, barium, beryllium, boron, cadmium, chromium, lead, selenium, and zinc) are mobilized and redistributed within the hydro-geochemical environment affected by the mining process. The elements are mobilized and dispersed only if they remain in solution, become complexed, or are agglomerated with colloidal or suspended material. Elements in solution will continue to be dispersed as long as the flow path carrying the elements remains acidic. A rise in pH will cause decreases in solubility and element concentration.

Complexes of major, minor, and trace elements associated with suspended colloids or particulate matter will move with the flow path as turbidity. An effective filter is necessary to remove the suspended matter and associated elements from the water.

Elements occurring in coal mine drainages have a variety of sources. Coals tend to have concentrations of antimony, arsenic, boron, barium, and selenium and to have local enrichments of cadmium and zinc; however, most of these occur in coals in quantities less than in their crustal abundances. In shale and clay components, higher concentrations of other elements may occur and form the source for another set of accessory elements.

The mining method, the geology of the coal seam, and the manner in which the geochemical systems are disturbed determine the variety and set of elemental sources that will be released to the environment. An underground mine, which disturbs primarily the coal seam, will release a different combination and concentration of accessory elements than will a surface mine that disrupts the total rock section overlying the coal.

In addition, certain elements have a preferred association with either the organic, sulfide, or mineral phase; the association also affects the manner of release and the pathway of element transport from the mine site. Elements such as germanium, boron, and beryllium tend to be complexed within the organic constituents of coal. As a result, the elements will be physically transported from the mine site with the extracted coal. On the other hand, if cadmium, copper, lead, and zinc, which are known to have sulfide phases associated with the coal, become oxidized at the mine site, they will become soluble and can enter the mine drainage network.

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Dominating all the mechanisms, however, is the leaching and chemical decomposition of the mineral phases by acid water. Under strongly acidic conditions, most elements are leached from the host rock and introduced into the mine drainage. When that occurs, the character of the acid mine drainage takes on a different dimension, and the environmental impact goes beyond one of acid, sulfate, and iron pollution.

#### Chemical Effects in the West

For the West, two types of hydrogeochemical systems are considered: (1) systems that become acidic as a result of pyrite oxidation, and (2) systems in which acid production, if it occurs, is neutralized as a result of the presence of calcite or dolomite in the overburden. Both types exist in the eastern United States but, with minor exceptions, only the second type has been identified in the West. In the West, where surface mining has potential to cause an increase in the dissolved solids of ground water but where significant pH decline is a rarity, the dominant change in dissolved solids is due to an increase in sulfate salts of calcium, magnesium, and sodium (i.e.,  $\text{SO}_4^{2-}$  increases are accompanied by increases in one or more of the three cations). Questions can be raised as to what level the increases can proceed and over what areas the water of increased concentrations can spread. In areas where  $\text{Ca}^{2+}$  is the dominant cation, the level to which  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  can rise is limited by the solubility of the mineral gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). In the absence of major concentrations of other cations and anions, the solubility constraint will limit  $\text{SO}_4^{2-}$  concentrations to less than 2,000 mg/l and  $\text{Ca}^{2+}$  concentrations to less than 600 mg/l. The total dissolved solids in the water will generally contain less than 3,000 to 3,500 mg/l, and the water will therefore be slightly brackish. Because of the high  $\text{SO}_4^{2-}$  content, such water will be unfit for human consumption or livestock use. Compared to natural ground water in many parts of the western United States, the concentrations are not particularly high and, in some areas, are lower than regional values. It is not uncommon for natural ground water to be saturated or near saturation with gypsum. In the Fort Union coal region, gypsum is commonly observed in overburden of bedrock and glacial types, and therefore, sulfate occurs naturally in the ground water.

In areas where the overburden deposits contain clay minerals and abundant exchangeable  $\text{Na}^+$  or  $\text{Mg}^{2+}$ , the  $\text{Ca}^{2+}$  concentrations in ground water are commonly much lower than would otherwise be the case because of the effect of cation exchange. The removal of  $\text{Ca}^{2+}$  by ion exchange enables the  $\text{SO}_4^{2-}$  content of the water to rise to higher levels because of the shift in status of the gypsum solubility constraint. In the West, sulfate values as high as 5,000 to 10,000 mg/l are observed in ground water affected by coal mining and, in some areas, in natural ground water. Even in those circumstances, the total dissolved solids of the water are rarely greater than 10,000 mg/l,